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Activated carbon from grapefruit waste.

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ACTIVATED CARBON FROM GRAPEFRUIT WASTE

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FOREWORD

This investigation was a project in the Division of Industrial Research of the University of Louisville. It was carried on in the Department of Chemical Engineering under the supervision of Dr. R. C. Ernst. The material in this thesis is of a confidential nature, as it was covered by a contractual arrangement with the donor of the fellowship, The Louisville Drying Machinery Company. It is not to be released for publication or to be placed on the shelves of the library except with the permission of the company and the approval of the Director of the Division of Industrial Research.

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ABSTRACT

The utilization of waste material from citrus canning plants constitutes a serious problem in both Texas and Florida. The purpose of this investigation was to devise a means of total utilization by the production of an activated carbon.

The experimental conditions, the use of solid catalysts, and the use of activating gases and steam were studied in an attempt to find the optimum conditions for the conversion of this material to active carbon. It was found that a carbon that compared very favorably with a high grade commercial decolorizing carbon could be produced from the material with steam activation at a temperature of about 950 Deg. C.

Work is now in progress on a pilot plant for the production of this material.

INTRODUCTION

The purpose of this investigation was to produce a commercially usable activated carbon from citrus waste material.

Activated carbon production has become an important industry because of the many ways in which the product may be used. Its most important use is in the refining of sugars and syrups. It is also used in decolorizing oils, fats, glycerine, alcholic beverages, various chemicals, and pharmaceuticals. This type of carbon also has the property of adsorbing odors and gases.

At the present time, the market for the dried cattle feed produced from the citrus waste disposal plants in both Florida and Texas is limited. As a high grade activated carbon had been produced from substances similar to grapefruit waste (6,8,11,14), it seemed reasonable to assume that the carbonization of the grapefruit waste would yield a carbon that could be activated.

A study of the conditions most favorable to the preparation of an activated carbon from this material was made.

HISTORICAL

The ability of charcoal to adsorb gases and to remove coloring matter from solutions, has been recognized for centuries. Little or no use was made of this property until the early part of the last century. About 1800, de Saussure (5) found that freshly heated beechwood charcoal took up gases to a remarkable extent, and appeared to condense them on itself. Several years later Hunter (5) became interested in the subject and repeated the experiments of de Saussure. The results of his experiments were not at all the same as those of de Saussure, these were undoubtly due to a difference in the method used to prepare the charcoal. Both found, however, that the charcoal adsorbed the more readily condensible gases to a much greater extent than the comparatively non condensible gases.

About 150 years ago Lowitz (5) demonstrated that charcoal had the power to deprive most coloring solutions of their color. A little later, in 1794, an English sugar refinery began using charcoal for decolorizing sugar liquors.

The success, in 1808, of beet sugar manufacture was largely due to the use of decolorizing charcoal. In 1810 Figuier (13) proved that bone char

possessed greater adsorbent properties than ordinary charcoal. In 1822 Payen (13) described a process of decolorizing beet sugar with the use of bone char. This method came into general use in both the cane and beet sugar industries, and in a great many cases is still used today.

The subject of activated carbon received but scant attention till the use of poison gas was commenced in the World War. At this time a great deal of research was done and methods were developed for the production of a highly active form of carbon suitable for the adsorption of this poison gas. Today there are commercial activated carbons on the market which possess as much as 50 times the adsorptive power of the older bone char.

One of the latest uses of activated carbon in this connection is for the purpose of water purification. In the Spring of 1930, the New Mulford, N. J., plant of the Hackensach Water Company demonstrated conclusively that powdered activated carbon could be used successfully and economically for the removal of tastes and odors from water. Since that time, over 1000 plants throughout the United States and Canada have used activated carbon for water purification(13). Along the same lines, activated carbons have been

used in sewage disposal, recovery of dry cleaners solvent, and recovery of gasoline vapors from natural gas.

Because of its ability to adsorb gases and vapors, activated carbon has been used in air conditioning equipment for the removal of such gases as hydrogen sulfide, sulfur dioxide, ethyl acetate and ammonia.

Still another use for activated carbon is in speeding up or catalyzing certain chemical reactions (13). In the capacity of a catalyst, activated carbon may act in either of two ways, both of which depend on the high adsorptive power of the carbon.

The oxidation of iodides to iodine with sodium nitrite takes place slowely, but the addition of activated carbon to the mass was found to cause the reaction to proceed very rapidly. Further study revealed that the carbon had merely adsorbed one of the products of the reaction, namely iodine, and thus allowed the reaction to proceed to completion. This acceleration was due to the familiar Le Chatelier-Braun principle. In other words, the carbon had acted to remove one of the bodies that had functioned as a negative catalyst (13).

The second way in which activated carbon may speed up a reaction is based on the fact that the carbon may adsorb preferentially the reactants to a much greater degree than the products. As a result, a very high concentration of the reactants is maintained at the surface of the carbon, thus allowing the reaction to proceed rapidly. As soon as the product is formed, it leaves the reaction zone. This is because the affinity of the carbon for the product is much less than for the reactants.

THEORETICAL

The theory of adsorption is extreemly complex and has never been completely or satisfactorily explained. It is usually considered to be a function of several factors; namely, surface action, electrical charges, and chemical activity.

It has been observed that a great number of both dissolved and colloidal substances tend to be attracted toward any surface. The total surface area of a cubic inch of a good grade of activated carbon has been estimated to be greater than 20,000 square yards (13). It is apparent that if a substance with this tremendous surface area is placed in a solution and then filtered off that a large portion of the solute will be removed with the carbon.

Many colloidal particles carry electrical charges. The carbon introduced, if it is charged oppositely, will attract the particles and neutralize the charge, thus forming a strong electrical bond between the two.

It has been found that activated carbons vary in their ability to adsorb certain substances. This difference appears to be a function of the activating process. The concept of chemical energy has been introduced to intepret these factors. It is believed that in the activating process tha carbon

acquires, what is called, free valences. These free valences are thought to have specific affinity for certain substances and tend to hold them with some type of physico-chemical bond.

Little is actually known of the true nature of activated carbon, but the theory which most satisfies the known facts is proposed by Dr. N. K. Chaney (4).

" Active carbon exists as a distinctive physical modification differing from other known inactive forms of carbon by some characteristic pecularity of molecular structure or arrangement. To this characteristic structure are attributed its special properties. It would be premature to assert that these two forms of carbon (active and inactive) are true allotropic modifications. It is not yet established that both forms are amorphus. This much is established: the two forms are characteristically distinct and easily differentiated, both by their properties and conditions of formation. In the absense of direct evidence, the presumption of the theory has beem that the active form would prove to be the simplest in structural form if not completely amorphus."

It has been experimentally proved that the elementary carbon formed by the breaking down of carbon containing substances may exist in either of two forms; namely, the active and inactive forms. The temperature of carbonization appears to be the controlling factor. The carbon deposited below 600 Deg. C. is active, while that deposited above 600 Deg. C. is inactive.

The active carbon, in order to be of value, must be separated from adsorbed and stabalized hydrocarbons which are associated with it. These hydrocarbons clog the pores and cover the surface of the active carbon in such a manner that its adsorptive powers are completely nullified. It must also be freed from any inactive carbon deposited on its surface by the decomposition of the hydrocarbons at a temperature above 600 Deg. C. The active carbon is rendered useful by a selective decomposition of the adsorbed hydrocarbons and inactive carbon adsorbed on its surface. From this discussion it is apparent that the manufacturing process is divided into two major parts. These are primary carbonization and activation. The primary carbonization is done by heating the material at a relatively low temperature to form the amorphus base carbon. The adsorbed hydrocarbons are then removed by heating to a much higher temperature in the presence of an activating agent.

The process of carbonization may be divided roughly into three steps:

(1) Complete drying and heating to 275-300 Deg.C.

(2) Exothermal decomposition

(3) Continued heating to 400-600 Deg. C.

In the carbonizing kiln, the temperature of

the material being carbonized will not rise to above 100 Deg. C. until it has lost all of its water. For rapid economical drying to the bone dry condition, the following factors should be considered: large exposed surface, good circulation, intimacy of contact, large temperature and humidity difference between gas and film surrounding the particle. After the free water is removed, with the material at approximately 100 Deg. C. and the gas at about 450-500 Deg. C., the material rapidly rises to 275-300 Deg. C. where exothermal decomposition begins. While heating to this temperature, water vapor, acetic acid, light oils, and traces of alcohol are evolved.

The conversion of cellulosic material to charcoal takes place at about 300 Deg. C., and is of an exothermal nature. Although the reaction does supply a certain amount of heat, it is but a small percentage compared to the total required for the whole carbonizing process. The bulk of the fixed gases liberated at this stage of the process is carbon dioxide. As the temperature of the material increases above 300 Deg. C. tars and heavier oils are released. Continued heating removes a greater and greater quantity of the tars. The density of the resulting charcoal varies directly as the tar content, as little

if any change of volume takes place after the exothermal decomposition. A great deal of the tar may be removed by simply continued heating, but the last traces are bound tenaciously to the surface of the active carbon, and their removal requires heating with an activating agent. This is the activation step.

The principles underlying activation are to so choose conditions as to decompose the hydrocarbons rapidly while the primary active carbon is oxidized slowely. This is a rather difficult thing to do since the hydrocarbons are bound so tightly to the carbon, and in many cases they are almost enclosed within the carbon particle itself. Air activation requires a temperature of between 350 and 400 Deg. C. while steam requires from 850 to 1,100 Deg. C.

Air activation has the advantage of operating at a comparatively low temperature, but the local overheating caused by the exothermal reaction causes an undue loss of primary carbon. In addition, there is a large loss in surface area of the residual carbon before the hydrocarbons are removed, hence carbons of the highest activity cannot be prepared in this way.(1)

Steam activation has the disadvantage of operating at a much higher temperature with its attendant engineering difficulties. But it has the great advantage of the endothermic reaction so that the hydrocarbons may be removed without excessive loss of the primary carbon. At elevated temperatures the following reaction takes place:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

It is very likely that this is the type of reaction that takes place in the steam activating process for the removal of the hydrocarbons. The elementary carbon is also decomposed with the formation of hydrogen and carbon monoxide:

$$C + H_2O \rightarrow CO + H_2$$

This reaction increases the surface area of the carbon by creating and enlarging fissures throughout the particle.

In theory, it would be possible to activate the carbon by removing the adsorbed hydrocarbons with some suitable solvent. This has been tried commercially but has met with very little success.

The most recent development in the activation of carbon has been the addition of certain chemicals (10) such as zinc chloride, calcium chloride or phosphoric

acid to the material being carbonized. Apparently, during carbonization these chemicals cause the hydrogen and carbon to be removed practically as water, no hydrocarbons being formed (1). According to Barker and Brown (2) these added chemicals act in the following manner:

During the activation process, the metallic chlorides, on being heated from 700 to 800 Deg. C. in the presence of carbon dioxide, is broken down to zinc oxide, and the chlorine liberated combines with the hydrocarbons present in the charcoal. At the higher temperatures, 800-900 Deg. C., the chlorinated hydrocarbons are broken down and liberated.

Carbon to be used for the purpose of decolorizing must be of a finely divided character to secure optimum results. This constitutes no serious problem, as it is possible to grind the product to a very fine state of subdivision in a ball mill. On the other hand, carbon to be used in gas adsorption must be granular, relatively dense, and non friable. Ray (12) states that:

" The desideratum for a gas adsorbing carbon is that it shall have the maximum adsorptive capacity per unit of volume rather than per unit of weight. This means that the largest mass of active carbon must be contained in unit space consistent with maintaining

free access or passageway to all the particles in such mass. In other words, the carbon must not be too dense or its permeability is destroyed, and it must not be too porus to the extent of needlessly sacrificing adsorbent material. If the density of the carbon falls below a critical minimum value, the adsorptive value per unit of space begins to be lost. The best gas adsorbent carbon is relatively dense. Activated coconut charcoal of maximum adsorptive capacity per unit of volume has an apparent density of approximately 0.66. A higher density than this indicates that the maximum surface is not exposed, and a lower density indicates that the carbon is traversed by larger pores and that the adsorptive capacity per unit of volume is decreased. Aside from the proper size and number of pores is the question of mechanical strength. Carbons that are to be used for industrial gas adsorption and vapor adsorption must be mechanically strong in order to resist the crushing and abrading action to which they are usually subjected."

Unfortunately, in the case of most vegetable materials, it is not possible to obtain a granular activated carbon of this density. Nevertheless, it is possible to produce this carbon synthetically. The initial unactivated carbon may be ground very finely and mixed with a plastic binder. When this mixed mass is subjected to a high pressure and extruded in the form of pellets and these pellets put through the activating process, the resulting product will have the required physical properties.

EXPERIMENTAL

Apparatus

The initial carbonization was carried out in a five gallon container that had been insulated with asbestos sheeting. Holes were punched in both the top and bottom of the container to allow circulation of the hot burner gases. The citrus waste was placed in quart containers and set in the bottom of the larger container, and the unit then set on a burner. A thermometer was placed in the top of the can so that the temperature of the gases could be kept below 350 Deg. C.

Activation was attempted by three different means; hence, three different types of apparatus were employed. In all cases, however, the heating was done by means of an electric muffle furnace capable of attaining a maximum temperature of about 1,100 Deg. C. By means of a tapped transformer in the circuit, it was possible to obtain 25 different settings, thus allowing close control over the temperature of the furnace.

The temperature measurements were made by means of a chromel-alumel thermocouple inserted into the rear of the furnace. The emf produced was measured with a special potentiometer. It should be observed

that the temperatures recorded are the temperatures of the furnace and not necessarily of the carbon in the bombs.

In the first stage, activation was attempted by the addition of an activating agent to the dried citrus waste, primary carbonization, and subsequent activation at high temperatures. For this activation, it was quite possible to use a rather small container. Hence, in order to speed experimental work, four 1½ by 6 inch stainless steel bombs were used in the furnace at the same time. These bombs were completely sealed on one end and threaded on the other. Caps for the bombs were made of stainless steel with a hole drilled and tapped for an 1/8 inch pipe in the center. These holes were to provide means of removal of the gases liberated during the process of activation. The pipes from each bomb were connected to one main outlet pipe which conducted the gases through the window and out of the building.

The bombs, when removed from the furnace, were at a very high temperature, sometimes as high as 1,050 Deg. C. At this temperature, any air would very quickly oxidize the carbon and very greatly reduce, if not completely destroy, the yield. Accordingly, a

gate valve was placed in the gas outlet pipe which could be closed and thus prevent exposure of the carbon to air.

When the use of catalysts alone failed to yield a satisfactory carbon, it was decided to try the effect of various gases; namely, air, steam, and chlorine. This required a somewhat larger and more complicated bomb than that previously described. As a shell, a 15 inch length of three inch diameter high pressure, cast-iron steam pipe was used. A fixed bottom was welded in one end of the pipe and the other end threaded for a cap. The cap had two holes drilled and tapped for a $\frac{1}{4}$ inch pipe. One hole was centrally located as the activating gas inlet and the other hole was located to one side to allow for the escape of the reaction gases.

To insure that the gases did not short circuit and go right out through the outlet without going through the carbon, it was decided to use a distributing manifold inside the bomb itself. This manifold was a piece of $\frac{1}{4}$ inch pipe the same length as the bomb. Very close to one end were drilled four small holes diametrically spaced on the pipe. The other end of the pipe was tapered in such a way that it would slip up and fit snugly in a coupling connected to the gas inlet on the cap when the cap was

screwed onto the bomb proper. In practice, the manifold was connected in this manner: The bomb was set in such a position that the open end was up. Next, the manifold was placed in the proper position and the primary carbon loosely packed around. This packing held the manifold in place so that the coupling could be screwed down and clamp the manifold in place.

As three different activating gases were experimented with, it was necessary to devise some method of determining the quantity of these gases used.

The chlorine was generated by the action of concentrated hydrochloric acid on manganese dioxide.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

The evolved gas was first passed through water in order to remove any hydrochloric acid which might have been present. (It would have been very destructive to the apparatus had any HCl been sent through at those elevated temperatures.) The gas was next conducted through concentrated sulfuric acid to remove any moisture which might have been

present in the gas. From here, the gaseous chlorine was conducted to the reaction bomb, the rate of evolution of chlorine being determined by the amount of heat applied to the generating flask. The quantity of chlorine to be used for the activation was determined, and the correct stoichiometric quantities of hydrochloric acid and manganese dioxide were placed in the reaction flask and allowed to react.

For the attempted air activation, the air was supplied to the reaction bomb by displacement with water from a 5 gallon bottle. In practice, two 5 gallon bottles were used. One was initially filled with water which was siphoned over to the empty bottle, thus forcing the air out of the bottle and into the reaction bomb. The bottle initially containing the air was placed on a balance so that at any time the weight of water run in could be determined. Consequently it was possible to determine the volume of air used in the experiment. By knowing the temperature of the air in the bottle and the barometric pressure (system operated at essentially barometric pressure), it was possible to calculate the weight of air used.

For the steam activation, the use of a flowmeter seemed impractical, and so a small boiler

was constructed in order that it could be weighed both before and after the run and from these figures determine the weight of steam used. For this purpose, an 8 inch length of 2 inch pipe was used. This was threaded on both ends and fitted with caps which afterwards were welded onto the pipe. Each cap was centrally drilled and tapped for a ¼ inch pipe. One hole was fitted with a plug to be used for filling the boiler and the other end fitted with a ¼ inch pipe to conduct the steam to the reaction bomb. When in use, the boiler was placed on a gas hot plate which served to generate the steam.

The reaction bomb itself, was fitted with a ¼ inch pipe line to carry away the gaseous products of the reaction. In this line was placed a valve to control the pressure in the bomb and a pressure gage.

As this method did not yield a carbon of the highest activity, it was decided to devise some means of agitating the carbon during the activating process. For this purpose, the same unit as described before was used with the addition of a stirring device. To accomplish this stirring, a rake with the same curvature as the inside of the bomb was constructed of a piece of ¼ inch steel plate. To this rake was attached

a steel rod about four feet long which extended outside the furnace. To prevent the escape of reaction gases in the furnace and a possible explosion, the rake handle exit was tapped and an 1/8 inch pipe fitted in so that it extended several feet outside the furnace.

Procedure

In all cases the raw material started with was either the straight dried or complete dried citrus feed. The dried feed is a result of the following process:

The waste, which constist of peel, rag, and seeds is taken from juice canning plants. It consists of from 85 to 88% of moisture. This material is first hammer-milled and then treated with a 10% lime slurry sufficient to give a resulting mass containing approximately 0.30% by weight of lime. This mass is then run into large semicircular cross sectional tanks in which it is throughly agitated. After running through this tank, the material is pressed to give a resulting solid of approximately 70% moisture. For the straight dried feed, the material is sent to a rotary tube drier where the moisture content is reduced to 10%. In this case the press liquor is sent to the sewer. However in the case of the complete dried feed, the press liquor is evaporated down and cut back into the solids before they are sent to the drier. The resulting product has therefore, a larger sugar content than the straight dried feed,

The experimental work may be divided into three divisions; namely, (1) activation with a solid activating agent, (2) activation with gaseous activating agents, and (3) activation with steam.

The first step in the process involving the use of a solid activating agent was the introduction of the agent. This was done in several ways; however; in each case the agent was placed in a water solution before introduction. The first means of introduction was simply throughly mixing the dried waste with the cold solution; second, mixing the dried waste with a hot solution; and third, heating the mass under a pressure of 15 pounds per square inch in a pressure cooker. This last method causes more complete penetration of the agent into the cells of the waste.

Next, the mass was placed in the quart cans with the lid ajar enough so that the evolved gases could escape but so as to prevent undue exposure to air and consequent loss of yield through oxidation. The cans were placed in the oven and carbonized at approximately 350 Deg. C., for an average of three hours. The resulting carbon was removed from the oven and weighed so that a yield on the primary carbon could be determined.

This primary carbon was then transferred to the bombs and thence to the furnace in which the temperature was brought up to a maximum in about five hours.

The bombs were then removed from the furnace and cooled. The resulting carbon was weighed for yield determinations. The carbon was boiled with dilute hydrochloric acid to remove both the activating agent and the natural ash in the material. This was then boiled with water, washed free of acid on the filter and subsequently dried.

The product was tested for both iodine adsorption and carbon tetrachloride retention. As the product was in a more or less lumpy form, it was necessary to pulverize it for the iodine adsorption test; however, for the carbon tetrachloride retention test, the material was tested in the lumpy form.

The activation with various gases was attempted with two modifications. These were, activation involving the auxiliary use of a solid activating agent along with the gas, and activation involving the use of an activating gas or steam only.

The method of initial carbonization was precisely the same as before. The mode of activation was similar except that the activating gas was admitted to

the bomb after it had reached the correct temperature. This temperature depended on the activating gas being used.

The last series of experiments were performed in an attempt to determine the effect of agitation on the rate of activation of carbon, with the idea that perhaps the required time could be considerably reduced. This procedure was exactly the same with the exception that the carbon was kept continually agitated by the means of a rake.

Testing of the Activated Carbon

The determination of the efficiency of a carbon is a function of several factors; namely, the nature of the carbon itself, the material being adsorbed and the conditions under which the material is being adsorbed. Carbon exhibits a rather selective nature; that is, certain types of carbon have specific affinities for particular types of bodies in different types of solutions. Therefore it is difficult, if not impossible, to develop a method for determining the universal efficiency of a carbon.

If it is desired to use activated carbon for a specific process, the only way of definitely predicting the success is to make a test on the actual material to be used. There is a rough correlation between the adsorptive powers of a carbon in different solutions, but it cannot be relied upon.

Our problem was not to develop a carbon for a specific purpose but to see whether it would be possible to activate the carbon produced from the grapefruit waste. The standard and most common test for the determination of the decolorizing efficiency of a carbon is the iodine adsorption test. This test is both rapid

and simple and gives reasonably good checks. Furthermore, it involves the use of a definite chemical and can therefore be reproduced at any time. For these reasons, it was decided to use the iodine test as a measure of the activity of these carbons. In this test, a good carbon should remove from 70 to 90% of the iodine in solution. For the purpose of comparison, "Nuchar C", a special, high grade, decolorizing carbon produced by the West Virginia Pulp and Paper Company, was used. The amount of iodine adsorbed by the carbon was divided by the amount adsorbed by the standard to arrive at an efficiency figure.

The details of the test as described by the "Modern Purifier" (13) are as follows:

Solutions and reagents:

Iodine solution: 2.7 grams of iodine per liter. Solution made by using a ratio of 1 part of iodine to 1.5 parts of KI, and distilled water.

Sodium thiosulfate: N/100

Sulfuric acid: 10% by volume

Starch indicator: 1% solution

Procedure:

Place 0.5000 grams of the carbon being tested in a 150 ml. beaker.

To this add 10 ml. of the sulfuric acid solution. Stir until the carbon is wetted and bring the mixture to a boil.

Allow to cool.

Add 100 ml. of the stock iodine solution to the carbon-acid mixture and immediately transfer the whole to another beaker of the same size and back six times, making twelve separate transfers.

Filter immediately through a quantitative filter paper in a gravity funnel and allow all the iodine solution to drain through the paper.

Stir the filtrate to insure homogeneity and then titrate 50 ml. with the N/100 sodium thiosulfate solution, using starch as an indicator.

Calculations:

Fraction of iodine removed is equal to the grams of iodine in the stock solution less the grams of iodine in the same unit volume in the filtrate divided by the grams of iodine per unit volume in the stock solution. The efficiency is equal to the fraction of iodine removed bybthe carbon sample divided by the fraction removed by "Nuchar C".

For studying the gas adsorbing properties of the carbon, the retention of CCl_4 was determined.

Briefly this consisted of passing CCl_4 vapor at a definite rate through a specific weight of the carbon. By means of a Y hooked in the gas line to a Bunsen burner, the gas from the carbon container was passed into the line. As long as only air passed out of the carbon container, the burner burned with a pale blue flame. However, as soon as the carbon became saturated with CCl_4, the vapor broke through and passed to the burner where it caused the flame to turn a brilliant green because of the presence of a copper coil in the flame.

In detail, the test was conducted in the following manner. Compressed air was first passed through two bottles in series containing concentrated sulfuric acid to remove any water vapor which might have been present. The dried air was then passed into two more bottles in series containing CCl_4 at a definite and constant temperature. This temperature was maintained at 0 Deg. C. by placing the two bottles down in a container filled with cracked ice. The air saturated with CCl_4 at 0 Deg. C. then passed through a calibrated orifice to which was hooked an inclined manometer filled with alcohol. From the orifice, the CCl_4 laden air was conducted to the carbon container which consisted of a glass tube $\frac{3}{4}$ inch wide and 5 inches long.

This container was loosely packed with five grams of the carbon and glass wool inserted in both ends to prevent the loss of carbon. One holed rubber stoppers were fitted over both ends and the carbon container connected to the line between the orifice and the burner. From here the air passed into the gas line of a Bunsen burner which was burning with the top of its flame in a copper coil. As long as the carbon adsorbed the CCl_4 vapors, the Bunsen flame remained a pale blue, but as soon as any CCl_4 vapor did break through, it was oxidized in the flame to free chlorine which in turn attacked the copper forming copper chloride which was volatilized with the liberation of an intense green flame.

DATA AND RESULTS

The waste was dried and completely carbonized for about three hours at a temperature of between 350 and 400 Deg. C., maximum. Yields of approximately 35% of primary carbon were obtained under these conditions. This yield was based on the waste alone without the addition of an activating agent. The exact conditions of the carbonization appeared to have no effect on the final product as long as the material was carbonized at a temperature below 600 Deg. C. Care was taken to insure that the material was completely carbonized before activation at a high temperature was attempted. If the material was not completely carbonized before, the inactive type of carbon would have been formed in the activation stage and would have decreased the activity of the final product.

The yields of activated carbon, in the case of the samples where a solid activating agent was used, are apparent yields. The value was obtained by dividing the total weight of the product by the weight of the grapefruit waste and catalyst used. This value is not the true yield of activated carbon, as a small amount of the unvolatilized activating agent remains in the sample. An analysis of a sample using 50% $ZnCl_2$, activated at 980 Deg. C. indicated that over 90% of the agent was volatilized.

Table 1 shows the experimental conditions and yields of activated carbon using zinc chloride as an activating agent. An examination of this table shows that the yield of activated carbon is approximately proportional to the activation temperature. This is as would be expected, for the oxidation of the carbon is more severe and the subsequent volitilization of the catalyst is more complete.

Table 2 shows the iodine adsorption efficiency and carbon tetrachloride retention of the samples as prepared in Table 1. This table indicates that under isothermal conditions, the efficiency of the carbon increases as the percentage of activating agent increases. The value of the percentage of activating agent to give optimum results, theoretically, should approach a definite value, and further addition of the agent should have no effect since it is the decomposition of the catalyst with the subsequent chlorination of the adsorbed hydrocarbons that produces the activity. After the hydrocarbons have been completely chlorinated and broken down, an excess of chlorine should have no effect. Apparently there is an optimum temperature for the activation process. The table indicates that up to a certain point the activity increases with increasing

Table 1

Experimental Conditions and Yields with $ZnCl_2$ as an Activating Agent

Sample #	% Activating Agent	Activating Temp. Deg. C.	Yield
1	9.1	770	34.2
2	16.7	744	34.2
3	16.7	832	31.9
4	23.0	778	34.6
5	28.6	786	37.0
6	28.6	978	26.6
7	33.3	786	35.5
8	33.3	1018	23.3
9	33.3	978	24.8
10	50.0	802	26.2
11	50.0	1018	19.0
12	50.0	978	33.4
13x	28.6	830	----
14x	33.3	830	----
15x	42.9	830	----
16x	50.0	830	----

x In the last four runs, the samples were activated for a period of 14 hours instead of the usual 5.

Table 2

Efficiency of Activation Using $ZnCl_2$ Activating Agent

Sample #	Gms. I_2/l in Std. Sol.	% Iodine Removed	Efficiency	CCl_4 Ret
1	2.1750	22.8	23.1	0
2	2.1750	26.9	27.5	0
3	2.1750	28.3	29.0	0
4	2.1750	25.9	26.5	0
5	2.2600	57.5	59.0	60
6	2.1850	43.0	44.2	64
7	2.2600	84.9	87.3	204
8	2.1850	66.9	68.5	125
9	2.1850	74.5	76.5	182
10	2.2600	94.5	97.1	305
11	2.1850	92.3	94.5	304
12	2.1850	84.0	86.0	291
13	2.1850	28.0	28.8	50
14	2.1850	67.0	68.8	192
15	2.1850	85.5	87.5	355
16	2.1850	93.0	95.5	472

temperature, but it begins to decrease if the temperature is increased further. The most active carbon produced in this group was at a temperature of 802 Deg. C. with 50% $ZnCl_2$ content. The last four runs were activated for 14 hours in order to determine the effect of increased time of activation on the resulting activity. Apparently this increased time of activation reduces the color adsorbing power but increases the CCl_4 retention ability. It was concluded that it was possible to produce a carbon of high activity by the use of a $ZnCl_2$ activating agent, but the amount of $ZnCl_2$ required would make the cost prohibitive.

In an effort to reduce the quantity of agent required, nickelic chloride and cupric chloride were investigated as possible activating agents. Tables 3 and 4 give the experimental conditions and yields. Tables 5 and 6 give the activity data for these experiments. These activity data are rather erratic and make an interpretation practically impossible. Nevertheless, the important conclusion may be drawn that it is impossible to produce a good activated carbon with sufficiently small amounts of either $NiCl_2$ or $CuCl_2$ to make the process commercially feasable.

Tables 7 and 8 give the experimental conditions and yields for activation involving the use

Table 3

Experimental Conditions and Yields with $NiCl_2$ as an Activating Agent

Sample #	% Activating Agent	Activation Temp. Deg. C.	Yield
17	2.9	970	21.3
18	4.8	744	25.7
19	4.8	832	24.8
20	5.7	970	25.3
21	8.3	970	27.5
22	9.1	770	30.2
23	10.7	970	27.7
24	20.0	978	25.9
25	23.0	778	30.0

Table 4

Experimental Conditions and Yields with $CuCl_2$ as an Activating Agent

Sample #	% Activating Agent	Activating Temp. Deg. C.	Yield
26	4.8	744	25.7
27	4.8	832	22.9
28	9.1	770	29.8
29	10.0	978	35.0
30	20.0	978	34.5
31	23.0	778	36.2

Table 5

Efficiency of Activation Using $NiCl_2$ Activating Agent

Sample #	Gms. I_2/l in Std. Sol.	% Iodine Removed	Efficiency	CCl_4 Ret.
17	2.2600	34.5	35.5	42
18	2.1750	16.6	17.0	0
19	2.1750	49.2	50.3	0
20	2.2600	48.0	49.3	37
21	2.2600	38.8	39.9	20
22	2.1750	15.4	15.8	0
23	2.2600	61.0	62.8	33
24	2.1750	13.2	13.4	0
25	2.2600	11.2	11.5	0

Table 6

Efficiency of Activation Using $CuCl_2$ Activating Agent

Sample #	Gms. I_2/l in Std. Sol.	% Iodine Removed	Efficiency	CCl_4 Ret.
26	2.1750	20.1	20.6	0
27	2.1750	21.9	22.4	0
28	2.1750	14.8	15.1	0
29	2.2250	28.6	29.6	0
30	2.2250	24.4	25.2	0
31	2.1750	20.2	20.7	0

Table 7

Experimental Conditions and Yields with H_3PO_4 as an Activating Agent

Sample #	% Activating Agent	Activating Temp. Deg. C.	Yield
32	4.8	832	24.8
33	9.1	770	31.0
34	16.7	744	32.5
35	23.0	778	34.0
36	28.6	786	35.0
37	33.0	786	35.2
38	50.0	802	24.7

Table 8

Experimental Conditions and Yields with $CaCl_2$ as an Activating Agent

Sample #	% Activating Agent	Activation Temp. Deg. C.	Yield
39	50.0	802	57.0

Table 9

Experimental Conditions and Yields with no Activating Agent

Sample #	% Activating Agent	Activating Temp. Deg. C.	Yield
40	None	802	32.0
41	None	1018	16.0

Table 10

Efficiency of Activation Using H_3PO_4 Activating Agent

Sample #	Gms. I_2/l in Std. Sol.	% Iodine Removed	Efficiency	CCl_4 Ret.
32	2.1750	36.4	37.2	0
33	2.1750	29.6	30.3	0
34	2.1750	30.8	31.5	0
35	2.2600	39.3	40.4	25
36	2.2600	37.5	38.6	40
37	2.2600	44.5	45.8	45
38	2.2600	65.3	67.3	170

Table 11

Efficiency of Activation Using $CaCl_2$ Activating Agent

Sample #	Gms. I_2/l in Std. Sol.	% Iodine Removed	Efficiency	CCl_4 Ret.
39	2.2600	53.0	54.5	30

Table 12

Efficiency of Activation Using No Activating Agent

Sample #	Gms. I_2/l in Std. Sol.	% Iodine Removed	Efficiency	CCl_4 Ret.
40	2.2600	19.3	19.8	0
41	2.1850	22.2	22.7	16

of phosphoric acid and calcium chloride respectively. The phosphoric acid treatment was hard on the equipment. Furthermore, under the conditions used it was impossible to produce a good activated carbon. Calcium chlorida as an activating agent was not thoroughly investigated, but a run made under the same conditions that produced maximum activity in the case of $ZnCl_2$ only produced a carbon of 57% activity as shown in Table 11; thereflre work was discontinued on this agent.

Table 9 shows the experimental conditions for special runs. Run 40 was made without the use of an activating agent but under the same conditions, otherwise, that produced a maximum activity in the case of $ZnCl_2$ activation. The resulting activity was only 19.8% which indicates that the $ZnCl_2$ increased the activity about 500%. Run 41 was made using boiling caustic soda to activate the carbon. The material was boiled with concentrated caustic soda both before and after activation; however, this appeared to have but little effect on the resulting activity.

Table 13 gives the experimental conditions for air activation. Increasing the activation temperature decreases both the yield and activity of the product. The explination of this fact is not evident but possibly it may be due to a selective oxidation of the

Table 13

Air Activation

Weight of air used was 25% of the weight of carbon used. No activating agent. Three hour carbonization at approximately 260 Deg. C. Three hours for Activation.

Sample #	% Yield	Act. Temp. Deg. C.	Gms. I_2/l in Std. Sol.	% Iodine Removed	Eff.
1	33.4	440	2.2250	27.2	28.1
2	14.6	560	2.2250	23.6	24.4
3	26.8	686	2.2250	21.3	22.1
4	25.8	778	2.2250	20.4	21.1
5	22.9	966	2.2250	19.1	19.8
6	28.9	970	2.2250	18.4	19.0

Sample #6 impregnated with 11.0% $ZnCl_2$ before carbonization.

carbon rather than the adsorbed hrdyocarbons. In this manner, as the yield was decreased the percentage of hydrocarbons would increase thus cutting down the activity. Sample 6 was treated with 11.0% $ZnCl_2$ before carbonization. This appeared to have no effect on the activity of the resulting product. It is possible that the air sweeping through the reaction bomb flushed the liberated chlorine from the bomb and prevented its reacting with the hydrocarbons.

The runs in Table 14 were made using various combinations of solid and gaseous activating agents. Nothing of particular importance is to be noted from these, except that a carbon of high activity was not prepared.

Table 16 shows the result of agitation on steam activation. In only 1/2 hour activating time, the activity reached a value which compared very favorably with the standard "Nuchar C". The agitation allowed more intimate contact between the steam and carbon thus making conditions more favorable for the reaction to occur. It is seen that the complete dried feed produced a slightly greater yield, but the activity of the product was somewhat lower than for the straight dried feed.

Table 14

Variable Experimental Conditions

Sample #	Carbonization Time, Hours	Activation Temp. Deg.C.	Remarks
1	22	940	Waste impregnated with 25% $CaCl_2$ under 15#/In.^{2} pressure and carbonized. Steam introduced, ratio 1# steam/1# carbon. 8 Hr. activation.
2	67	940	11.1% $ZnCl_2$ added to waste before carb'n. Activated 8 hours, ratio 1# steam/ 1# carbon.
3	4½	940	No solid activating agent. 6 Hr. Act. 4.2% Cl_2 and 1# steam/1# carbon.
4	22	960	Waste impregnated with 17.3% $ZnCl_2$ under 15 #/ sq. in. pressure and carbonized. 4 Hr. activation. A slow stream of Cl_2 run thru for ½ Hr. followed by CO_2 for ½ Hr.
5	42	960	No solid activating agent. 6 Hr. Act. with 1 # steam/ 1 # carbon
6	42	960	No solid activating agent. 6 Hr. Act. with 2# steam/ 1# carbon following 4.2% Cl_2.
7	8	940	No solid activating agent. 2½ Hr. Act. with 1# steam/ 1# carbon.
8	6	970	No solid activating agent. 5 Hrs. Act. with 1# steam/ 1# carbon.

Table 15

Samples Activated as Indicated in Table 14

Sample #	% Yield	Gms. I_2/l in Std. Sol.	% Iodine Removed	Efficiency
1	37.9	2.0200	46.3	47.5
2	24.8	2.0200	53.2	54.5
3	----	2.0200	48.7	50.0
4	28.7	2.0200	31.0	31.8
5	21.0	2.0200	46.5	47.7
6	19.2	2.0200	46.8	48.1
7	22.5	2.0200	35.9	36.8
8	18.0	2.0200	34.6	35.5

Table 16

Steam Activation Involving Agitation

Experimental Conditions

A Complete dried feed, agitated and activated with steam for ½ hour. Yield--17.5%. Act. Temp. was 950 Deg. C.

B Straight dried feed, agitated and activated at 950 Deg. C. with steam for ½ hour. Yield---10.9%

C Check of "B". Yield--12.0%

Results

Sample #	Gms. I_2/l in Std. Sol.	% Iodine Removed	% Efficiency
Nuchar	2.2340	97.1	100.0
A	2.2340	87.0	89.6
B	2.2340	96.5	99.4
C	2.2340	92.6	95.4

CONCLUSIONS AND RECOMMENDATIONS

From the observed data, it was concluded that it was possible to produce a good grade decolorizing carbon from the dried grapefruit waste. Of the various methods attempted, the best by far was found to be steam activation at a temperature of 950 Deg. C. with continual agitation of the carbon. Under the experimental conditions used, the process was carried out in ½ hour. As the agitation was not very effective, it is quite possible that this time may be cut down in a commercial or pilot plant unit where the agitation would be more effective.

At the present time the process is in the pilot plant stage. A kiln has been built by the Louisville Drying Machinery Company and runs are now in progress to determine its operating characteristics and general fitness for the production of activated carbon. For the purpose of economy the same unit is being used in both the carbonizing and activating stage.

Figures 1 through 4 show details of the pilot plant unit. The center of the unit is a seven foot tube 15 inches in diameter made of a special alloy cast iron. This tube is enclosed by a fire brick furnace with an arrangement of baffles so that there are two complete passes of the hit burner gases. A 2 inch shaft runs down the axis of this tube with agitation paddles located of three inch centers. This shaft is driven at 20 rpm by a 5 hp

motor and two speed reducers. As shown in Figure 1, the feed enters the cold end of the tube through a sheet metal chute having two slide valves in series. The material runs through the tube and discharges into a special sheet metal box.(Fig. 4) bolted onto the hot end of the tube by means of wing nuts. These precautions are taken so that a minimum of air will be admitted to the kiln when it is in operation. A steam inlet is located in the hot end of the tube and provision for the removal of the reaction gases is made at the feed end (Fig. 1) of the tube. The furnace is fired with a gas burner, and the flue gases are removed by means of a fan blower and venturi in the stack pipe.

Figure 5 is a flow sheet of the proposed process which is the ultimate aim of this investigation.

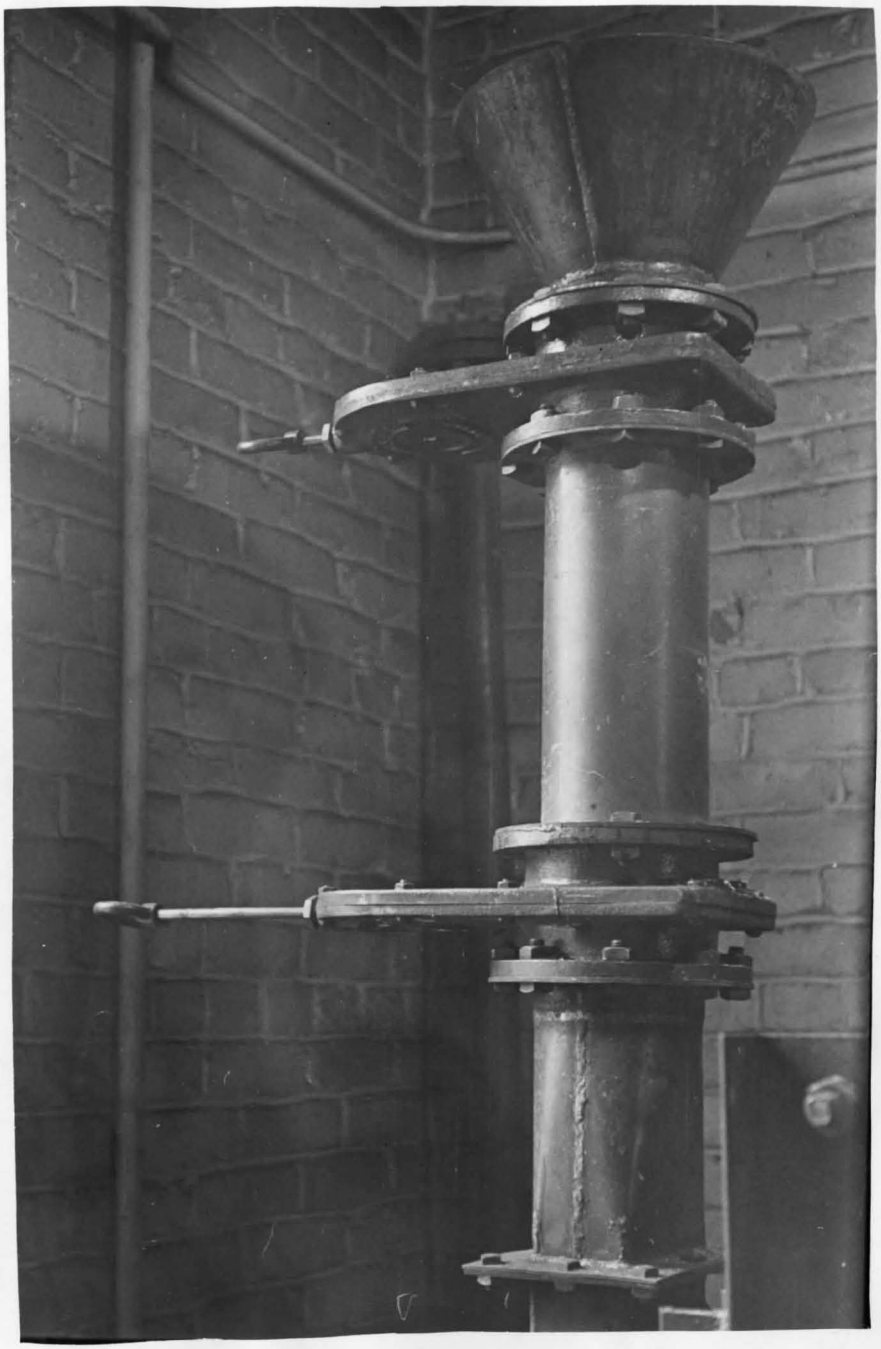

Figure 1

Raw Material Feed Pipe to Activator

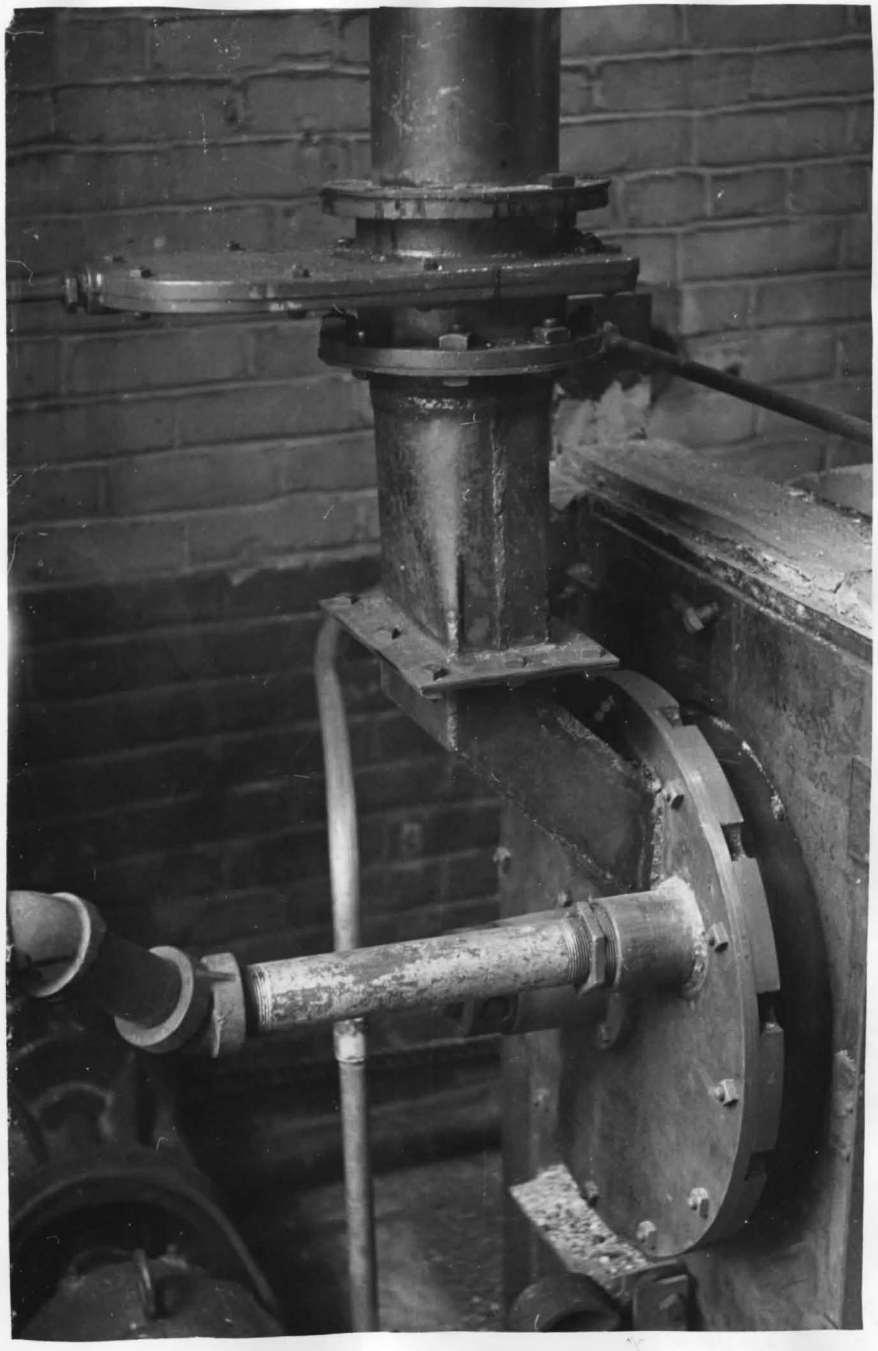

Figure 2

Details of Inlet End Showing Reaction Gas Outlet

Figure 3

Overall View of Furnace

Figure 4

Details of Discharge End Showing Steam Boiler

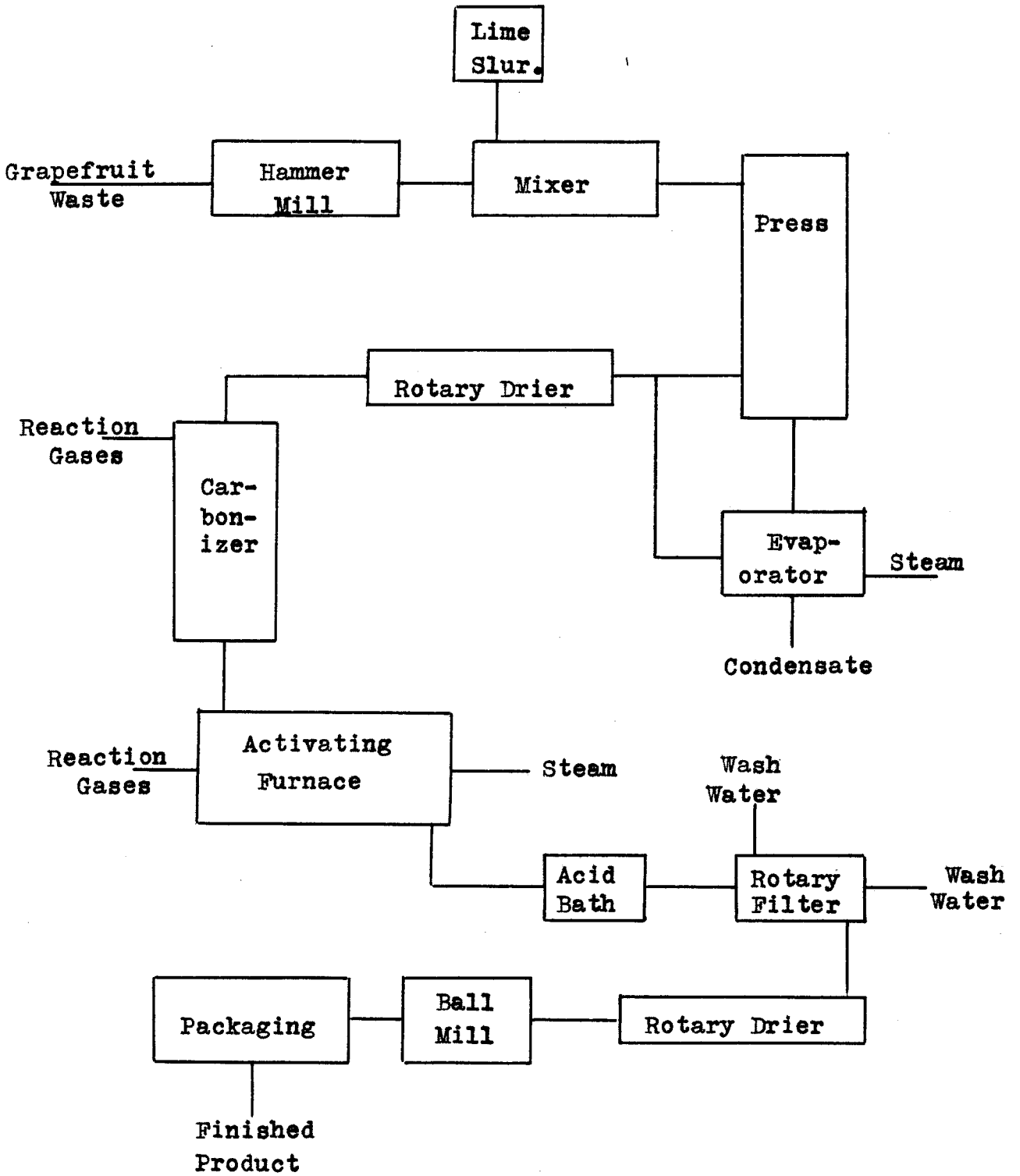

Figure 5

Activated Carbon Flow Sheet

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